APPLICATION OF SMALL SCALE EXTRACTIONS TO LARGE VOLUME INJECTIONS FOR ENVIRONMENTAL GC/MS ANALYSIS

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ABSTRACT:

Pollution prevention initiatives and OSHA regulations have pushed for development of analytical techniques that use less solvent. Field analysis is normally hampered by lack of bench space and time. Using small scale or micro extractions coupled with large volume injection (LVI) is one solution for all of these problems.

This investigation explores the use of simple test tube extractions coupled with 100 µl injections to reduce sample, solvent, and time for Semivolatile GC/MS analysis. This method uses 10 ml of sample, 1-2 ml of solvent, and minutes to complete instead of hours or days. Over 120 analytes are tested from EPA method 8270[1]. The wide range of volatility presented by these analytes made the PTV technique difficult, but acceptable results were achieved for the vast majority. Recovery and precision data are presented for DI water, groundwater, and wastewater as compared with separatory funnel extractions.

INTRODUCTION:

Programmable Temperature Vaporizers, or PTV inlets, allow for the injection of larger volumes of solvent extract into GC and GC/MS systems. Injecting larger volumes can

increase the sensitivity of the instrument proportionally by the increase in volume injected. This means that a 100 µl injection can increase the sensitivity of the instrument by 100 times over a standard 1 µl injection.

Using this technique, smaller volumes of sample can be extracted to achieve the same detection limit as the smaller injection method. Standard water extractions for EPA semivolatile methods[1,2,3,4] require the extraction of 1000 ml of sample, using 1-2 µl injections for analysis. Extracting 10 ml of sample followed by analysis using a 100 µl PTV injection would theoretically yield the same detection limits as the standard technique, but with great benefits to lab and field operations (table 2). The small-scale extraction would

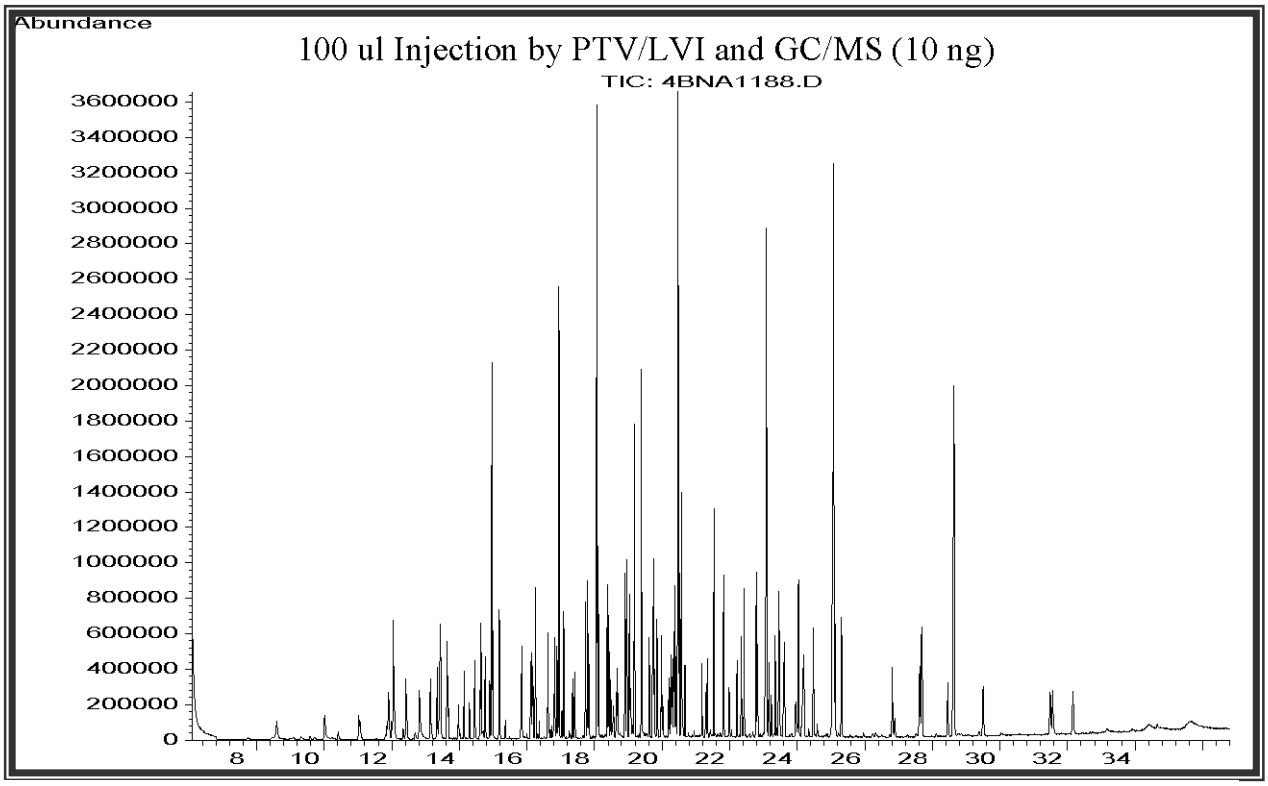

Figure 1: Chromatogram of 146 semivolatile analytes extracted (acid/base). from 10 ml of water at 10 µg/L

[d] The EPA does not endorse any products mentioned in this paper. Opinions expressed are of the authors only.

allow reduction in sample collection costs, extraction time, labor, reagent cost, and critical bench space.

In this, our most current study, we build on our previous work[5,6,7,8,9] and further investigate a PTV/small volume extraction method for the pesticide and semivolatile analytes found in method 8270[1]. The matrices currently under investigation include DI water, groundwater, and wastewater. The small-scale extractions employed used 10 ml aliquots of sample extracted with 1-2 ml of methylene chloride in a simple 15 ml centrifuge tube. No concentration method was required. All samples were spiked at a low level of 10 µg/L for the purpose of method detection limit (MDL) estimation[10]. Comparison extractions were performed by separatory funnel (EPA method 3510[1].

TABLE 1: PTV PARAMETERS FOR GERSTEL CIS-4 WITH MULTI-INJECTIONS

Injection Volume	10 µl (using 50 µl syringe)
Number of Injections	10 (total volume 100 µl)
Delay between Injection	5 seconds
Injection Time	1.91 minutes
Split Time	2.15 minutes (~ 0.2 minutes after injections complete)
Inlet Temp	-5^{0} C (hold until 2.16 minutes or longer than split time)
Inlet Ramp	300^{0} C/minute until 300^{0} C, hold for run
Splitless Time	from 2.11 until 3.55 minutes (~0.4 minutes after 300^{0} C reached)
Vent Flow	200 ml/minute (flow through inlet during evaporation of solvent)
Split Flow	100 ml/minute at 3.55 minutes (to remove matrix from inlet)

These final PTV parameters were not used throughout the entire study. Physical and chemical changes in the inlet can affect the evaporation rate of the solvent. Therefore, small changes were made from time to time to optimize analyte recovery and chromatography.

RESULTS:

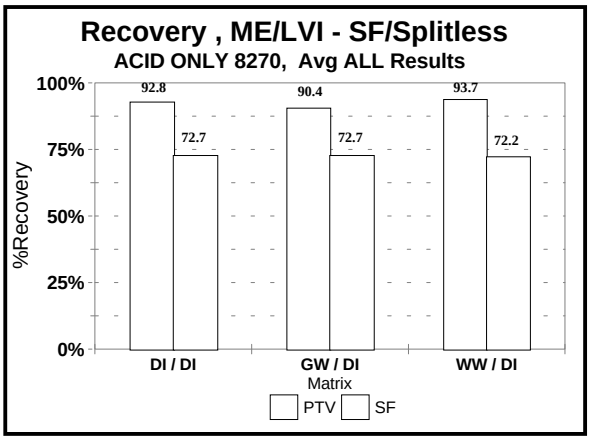

Chart 1: Average recovery data for all analytes and all replicates for the acid only extractions.

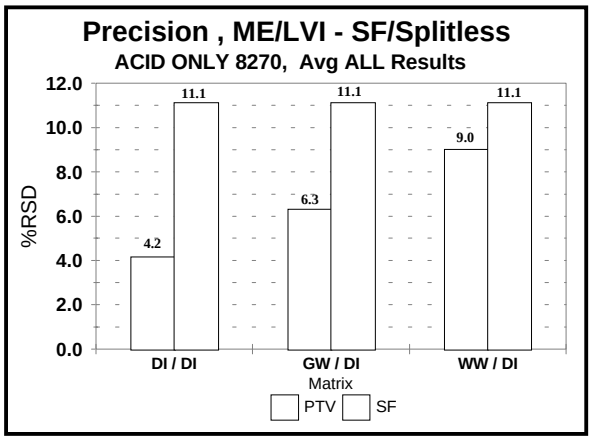

Chart 2: Average precision data for all analytes and all replicates for the acid only extractions.

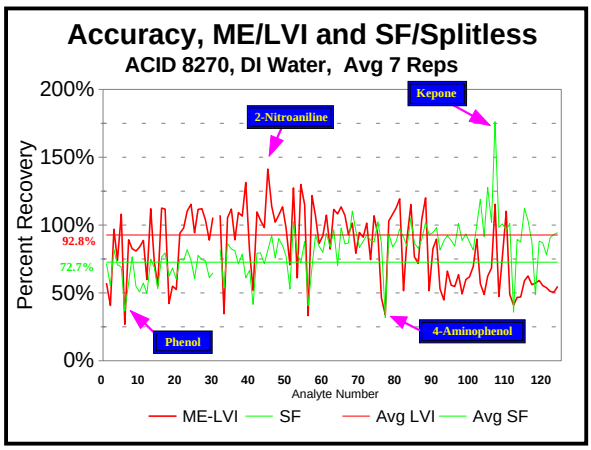

Chart 3: Average recovery data for individual analytes and all replicates for the acid only DI water extractions (best results).

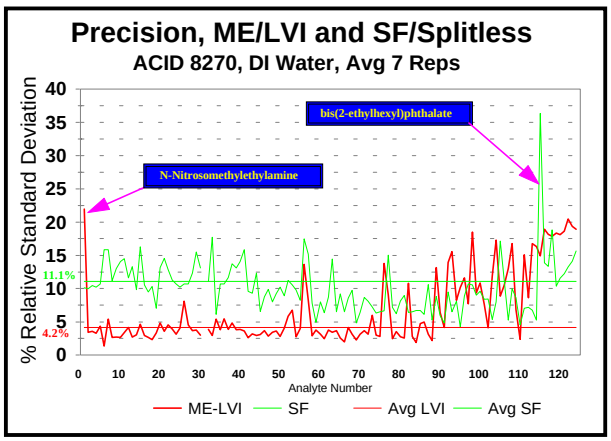

Chart 4: Average precision data for individual analytes and all replicates for the acid only extractions.

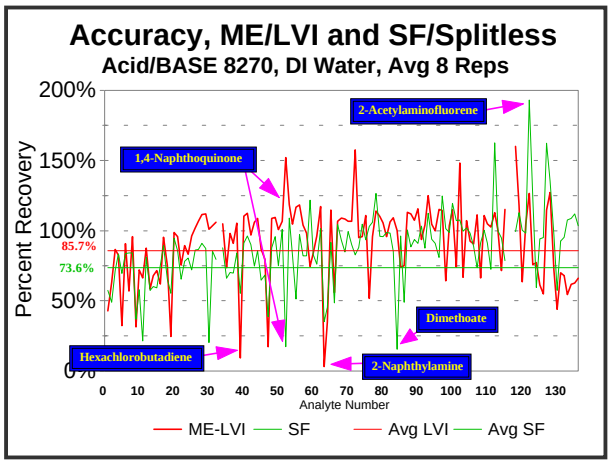

Chart 5: Average recovery data for individual analytes and all replicates for the acid/base DI water extractions.

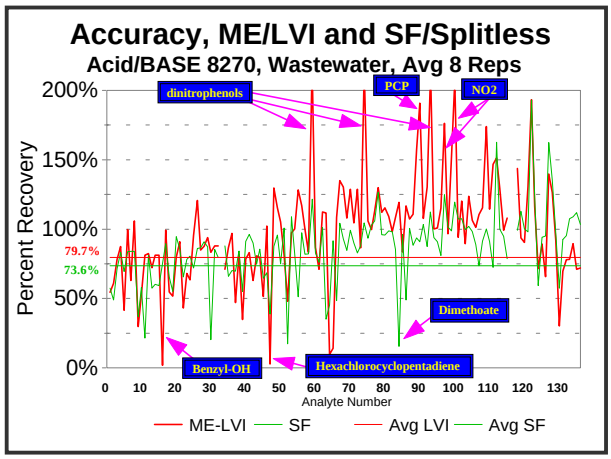

Chart 6: Average recovery data for individual analytes and all replicates for the acid/base wastewater extractions (poorest results).

DISCUSSION:

The following table (table 2) compares the differences for time and volume between the two techniques:

TABLE 2: METHOD COMPARISON FOR 7 EXTRACTIONS
(Conventional verses Micro-extraction PTV/LVI)

	Conventional	**Micro PTV/LVI**
Sample Amount	1000 ml	10 ml
Extraction Time	5 – 24 hr.	30 – 45 min
Concentration Time	30 – 120 min.	0 min
Solvent Used	100 – 600 ml	1 ml
Injection Amount	1 µl	100 µl
Waste Generated	1 – 30 L	10 – 700 ml

There are some difficulties with PTV. If too much of the solvent is vented during injection, some analytes will be carried away[11]. If not enough solvent is vented, then two

problems could arise. One is that flooding occurs in the inlet and liquid solvent drips out the vent with the analytes (too rapid rate of injection). The other is that flooding occurs on the head of the GC column (vent time too short to remove most of solvent) and chromatography suffers[12,13].

Reactivity of compounds is more of a concern with PTV than conventional split/splitless GC because of how long the analytes stay in the inlet. Large amounts of injected extract increase the possibility of suspended particles accumulating in the injection port, which could promote the degradation of analytes[14]. Therefore, it is imperative that the least reactive packing be used in the liner, such as fused silica wool. It is also important that the liner be packed consistently to avoid re-optimization of PTV parameters due to changes in evaporation characteristics[11].

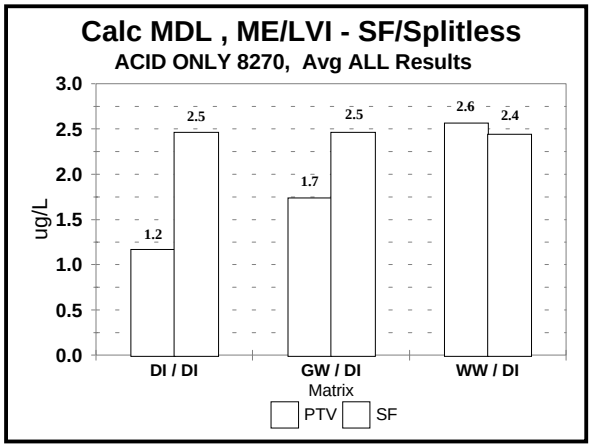

Chart 7: Average MDL data for all analytes and all replicates for the acid only extractions.

CONCLUSIONS:

The results indicate this should be a viable technique for both field and lab use, but there may be some difficulty with dirty samples. Adequate detection limits are achievable for most purposes (Chart 7). Centrifuging the sample and extract to ensure separation of phases greatly improved recoveries and precision. This technique requires an operator that understands split/splitless injection techniques very well, especially PTV. It has a

tremendous amount of potential for revolutionizing productivity in the laboratory through reduced-scale extractions. Less solvent is used for extraction and would therefore make it easier to conform to OSHA's lower exposure limit. The simple extractions require very little bench space or time to perform, making it very suitable for mobile field or fixed lab use.

References:

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[2] 40 CFR 136, appendix A, *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.*

[3] EPA Contract Lab Program, *Statement of Work*, OLM03.0

[4] EPA Publication 600/4-88/039, *Methods for the Determination of Organic Compounds in Drinking Water.*

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[8] R. McMillin, D. Gregg, M. Daggett, J. Thorp, "Application of Small Scale Extractions to Large Volume Injections for Semivolatile GC/MS Analysis", #160, *Final Program of the 92nd Meeting Gulf Coast Conference*, Galveston, TX., Sept. 1997.

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[10] 40 CFR 136, appendix B, *Definition and Procedure for the Determination of the Method Detection Limit*

[11] Ians G.J. Mol, Hans-Gerd Janssen, Carel A. Cramers, Udo A.Th. Brinkman, "Large Volume Sample Introduction Using Temperature Programmable Injectors: Implications of Liner Diameter", *Journal of High Resolution Chromatography*, Vol. 18, Jan, 1995.

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[13] K. Grob, Jr., J. Chromatographic Science, **213** (1981) 3.

[14] S. Muller, J. Efer, W. Engewald, "Gas Chromatographic Water Analysis by Direct Injection of Large Sample Volumes in an Adsorbent-Packed PTV Injector, *Chromatographia*, Vol. 38, No. 11/12, June 1994